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IN POLYPHOSPHAZENES

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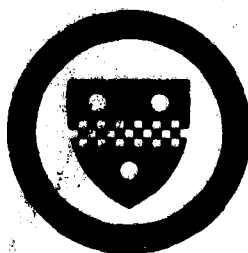## Pittsburgh, Pennsylvania 15261

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Unoriented and oriented samples of two phosphazene homopolymers with chemical structure $[NPX_2]_n$, where $X = CF_3CH_2O$ and $p-CH_3C_6H_4O$, and three unfilled and filled alkoxy-type polyphosphazene copolymers, plus one filled aryloxy-type copolymer were examined using a Rheovibron viscoelastometer. Measurements were made from $-120°C$ to temperatures above the $T(1)$ transition of the respective polymers. The effects of orientation and repeated temperature cycling through the $T(1)$ transition temperatures were studied. The overall physical behavior of these polyphosphazenes was dominated by changes

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that occurred through the primary softening dispersion and the so-called mosomorphic or T(1) transition region. The enthalpy of the T(1) transition, and the T(1) temperature were investigated by differential scanning calorimetry (DSC) as a function of temperature cycling through the T(1) region. For instance, the change in enthalpy through the T(1) region is about an order of magnitude larger than it is at Tm for the unfilled polyphosphazene homopolymers. The Tg's of the polyphosphazenes were also determined. Density measurements were made on oriented and unoriented specimens using a floatation method. Although an increase in density (and crystallinity) was observed when specimens were cycled through the T(1) transition, no significant difference in density was found between oriented and unoriented materials. Some discussion of the molecular origin of the T(1) mesophase transition is included.

Key words: 1. Polyphosphazenes (homo and copolymers)
            2. Dynamic Mechanical Properties
            3. Thermal Transitions
            4. Orientation
            5. Density

SYNOPSIS

Unoriented and oriented samples of two phosphazene homopolymers with chemical structure $[NPX_2]_n$, where $X = CF_3CH_2O$ and $p-CH_3C_6H_4O$, and three unfilled and filled alkoxy-type polyphosphazene copolymers, plus one filled aryloxy-type copolymer were examined using a Rheovibron viscoelastometer. Measurements were made from $-120°C$ to temperatures above the T(1) transition of the respective polymers. The effects of orientation and repeated temperature cycling through the T(1) transition temperatures were studied. The overall physical behavior of these polyphosphazenes was dominated by changes that occurred through the primary softening dispersion and the so-called mosomorphic or T(1) transition region. The enthalpy of the T(1) transition, and the T(1) temperature were investigated by differential scanning calorimetry (DSC) as a function of temperature cycling through the T(1) region. For instance, the change in enthalpy through the T(1) region is about an order of magnitude larger than it is at Tm for the unfilled polyphosphazene homopolymers. The Tg's of the polyphosphazenes were also determined. Density measurements were made on oriented and unoriented specimens using a floatation method. Although an increase in density (and crystallinity) was observed when specimens were cycled through the T(1) transition, no significant difference in density was found between oriented and unoriented materials. Some discussion of the molecular origin of the T(1) mesophase transition is included.

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                     2. Dynamic Mechanical Properties

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I. INTRODUCTION

Conventional synthetic organic polymers usually consist of long chains comprised of carbon backbone atoms or even carbon atoms linked through oxygen and/or nitrogen atoms. The "organic" nature of such polymers is to be partly responsible for some of their weaknesses in properties. Many of these materials are flammable, tend to melt or oxidize and char at high temperatues. Most of these macromolecules dissolve or swell in hydrocarbon fuels and solvents, which restrict their utility as engineering materials. Very few of them remain flexible down to low temperatures. Only a few of these synthetic polymers are compatible with the human body and can be used in prosthetic devices such as artificial heart pumps, replacement blood vessels, artificial kidneys, etc.

In an effort to overcome some of these deficiencies encountered in conventional organic polymers, two main types of "inorganic" backbone polymers have been developed. One of these contains silicon in the chain backbone and forms a class known as poly(organosiloxanes). Presently some are used in applications where stability, flexibility, and biomedical compatibility are needed. The other class is the poly(organophosphazenes) which have alternating phosphorus and nitrogen atoms in the backbone as illustrated in Figure 1. Developments and some related research activities in this area have been reviewed by Shaw[1,2] and Allcock[3,4]. The details of polyphosphazene synthesis are given in references 5 and 6. Polyphosphazene synthesis is unique in that a large variety of polyphosphazenes, all with different properties, can be prepared from one precursor, poly(dichlorophosphazene), by reacting it with other selected reactants such as alcohols, phenols and amines. Thus far, more than 60 polyphosphazenes have been synthesized in this way and even more novel alkyl and aryl substituted polymers have now been prepared[7]. Some important properties of many of these materials are given in references 8 and 9.

In general, when only one type of substituent group is present, the polymers are invariably semicrystalline, thermoplastic materials, but when two or more types of substituent groups are introduced (mixed substituent polymers), crystallinity is often inhibited to the point where only rubbery, amorphous materials are obtained[10], except perhaps where the two substituents are present in about equal amounts[11].

The technological focus of phosphazene polymer research is predicted upon applications where other polymers are deficient or even unsuitable. Applications fall into three broad categories, namely (a) special service elastomers; (b) fire-resistant elastomers and plastics; (c) biomedical engineering applications. For instance, in group (a), fluoroalkoxy-type polyphosphazene elastomers (PNF) exhibit unusual resistance to oils, solvents and hydraulic fluids. In addition. they possess low-temperature flexibility ($Tg = -60 \sim -80°C$) as well as high-temperature stability. Through the proper choice of side groups, poly(fluoro-alkoxyphosphazenes) can be designed to have serviceability in the range from -60°C to 200°C or even higher. The poly(fluoroalkoxyphosphazene) copolymers are fairly tough, rubbery materials with tensile strength of 1080 to 1490 psi and elongation from 150 to 280 percent or more[12]. These materials find uses such as O-rings, lip-seals, arctic fuel hoses, gaskets, and in coated fabrics[13-16]. A wide variety of polyphosphazenes including rigid plastics, elastomers, flexible films, and expanded foams have been developed approaching commercialization in recent years.

In category (b), most organic polymers either burn rapidly in air, some often evolving excessive amounts of smoke and toxic gases. The unfilled poly(arlyoxy-phosphazenes) are self-extinguishing in air under normal test conditions. They have relatively high limiting oxygen indices (i.e. LOI values)[17] which can be raised as high as 65 when suitable fillers are incorporated in the polymer

matrix. It has been established recently, that they evolve low to moderate levels of smoke[18] and toxic gases[19,20] compared with many other commercially available polymers. Generally, it is found that both the flammability and the smoke density of polyphosphazenes can be further reduced by using inert fillers[18,21,22]. Flame retardant foams and wire coverings feature amongst the most promising applications for poly(aryloxyphosphazene) copolymers[23,24] currently under evaluation. In category (c), some polyphosphazenes are also found to have potential as body organ replacements. Some show promise too, as bio-degradable polymers[8,25]. Water soluble materials such as poly(aminophosphazenes) can function as carrier molecules for the controllable release of chemotherapeutic drugs[8,25] in biological systems.

Many crystalline polyphosphazenes characteristically exhibit two first order transitions[9] sometimes separated by a temperature interval often as much as 150 to 250°C. The lower of these transitions, T(1), corresponds to a transformation from a crystalline to a mesomorphic state[9,26]. The upper transition, Tm, represents the true melting point where an isotropic melt results.

In the present work, we will deal with the behavior and nature of the transitions at T(1) and Tm as revealed by thermomechanical measurements (Rheovibron), density (floatation method) and calorimetric (DSC) measurments. Although dynamical mechanical spectra have been reported using torsional braid[27] and torsion pendulum techniques, the present study focuses on new information in dynamical mechanical behavior in regards to polymer chemistry, filler type and to pertinent property changes that depend upon temperature and sample orientation.

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*Recent unpublished work by Plazek and associates has demonstrated that in torsional braid analysis two spurious peaks can be observed in the log decrement curves when the material itself does not exhibit anything.

II. EXPERIMENTAL

1. Materials

The polymers used in this work were obtained from Dr. Allcock's laboratory at Penn State University, Dr. R. Singler of the Army Materials and Mechanics Research Center, Watertown, Massachusetts, and from Drs. David Tate and David Lawson, Firestone Tire and Rubber Company, Akron, Ohio.

Materials are listed in Tables 1 and 2. Samples 1 and 2 are semi-crystalline hompolymers. Samples 3 through 6 are unfilled and filled hybrid copolymers. All polyphosphazene samples were of high average molecular weight ($\overline{Mw} \geq 10^6$) with broad molecular weight distribution (sometimes $\overline{Mw}/\overline{Mn} > 10$)[26].

Samples 1 and 2 initially obtained in the form of unoriented films, were also drawn to about X10 and X3.5 respectively, in order to investigate the effects of molecular orientation on their dynamic mechanical properties and T_g values. Sample 1 was drawn at 70°C (which is just below T(1)) and Sample 2 was cold-drawn at room temperature. Fabrication by molding at higher temperatures via melt crystallization invariably tended to induce brittleness in these films or fibrilation in oriented samples so they were not further studied.

2. Rheovibron Dynamic Viscoelastometer

Dynamic mechanical properties were measured with a Rheovibron Model DDV-II (manufactured by Toyo Measuring Instruments Company, Japan). The storage modulus, E', loss modulus, E" and loss tangent (tan δ) of the polymers were obtained as a function of temperature (often in the range -120° to 180°C approximately) at 3.5 and 110 Hz using heating and cooling rates of 1°C/min. Liquid nitrogen was used as a refrigerant for subambient temperature work. In subambient measurements, moisture was excluded from the specimens by means of a transparent

plexiglass box that fitted over the instrument and which was purged continually with dry air or nitrogen during sample equilibration and measurements.

3. Differential Scanning Calorimetry

A Perkin-Elmer DSC II calorimeter with a scanning auto zero and a mini-computer was used to measure transition temperatures and to determine their respective heats of transitions. The effects of thermal history on these enthalpies of transition and transition temperatures were investigated by scanning as many as 9 to 10 cycles sometimes.

For T_g measurements, liquid nitrogen was used as a coolant in the DSC apparatus. Heats of transitions were determined by computerized integration of the areas under the DSC curves using indium as a reference material. The instrument temperature was calibrated using standard samples.

4. Density Measurement

Density measurements on unoriented and oriented samples of 1 and 2 were carried out by the well-known floatation method using CsCl aqueous solution. The temperature of measurement was 24°C. Beginning from a rather dense CsCl solution, small amount of distilled water was added to the solution from time to time, with proper mixing, until the density of a test specimen matched exactly the solution density. Then, the density of this solution was determined with a pycnometer, which gave the sample density.

III. RESULTS AND DISCUSSION

1. Dynamic Mechanical Behavior

Data dealing with mechanical properties of polyphosphazenes are sparse and sometimes conflicting. In the present experiments, the storage Young's modulus, E', the loss modulus, E" and the loss factor tan δ of the samples were obtained from measurements in temperature interval from -120°C to temperatures sometimes as high as 200°, where the samples became too soft to make accurate measurements.

Results of E', E" and tan δ versus temperature obtained for these
polyphosphazenes at 110 and 3.5 Hz are shown as curves in Figures 2 through 13.
All curves are corrected for clamping and other instrumental contributions using
the method outlined by Massa[28] several years ago, (see Appendix I). For all
of the samples the absolute values of E*, the complex modulus, lie so close to
the E' curves that they are omitted in these figures.

The dynamic mechanical response of unoriented poly[bis(trifluoroethoxy)
phosphazene] is illustrated in Figure 2 (1st run) and Figure 3 (7th consecutive
run). Typical plateau values of E' (approximately 10^{10} dynes/cm^2) are shown in
Figure 2 for the glassy region. Above the primary softening dispersion region,
E' decreases rapidly to a value of about 2×10^9 dynes/cm^2, which lies much
higher than the $\sim 10^7$ dynes/cm^2 value usually encountered in amorphous rubbery
polymeric materials. Relaxation behavior associated with any glass transition
is termed a primary softening dispersion in this paper. This higher value
arises because of the crystalline nature of this polyphosphazene. About 80°C
a T(1) transition is apparent. This transition sets an upper temperature limit
for polyphosphazenes as useful engineering materials. It also provides a con-
venient lower temperature limit where the material can be easily compression
molded.

Crystallinity develops upon cycling the polymer up and down through T(1),
(see "Differential Scanning Calorimetry" section) as witnessed in Fig. 4, through
the increase in E' and a concomitant decrease in the height of the primary
softening dispersion peak in the tan δ curves. The decrease in peak height
and in peak area corresponds to a reduction in the amorphous component of the
polyphosphazene (i.e., an increase in the crystalline fraction) of this polymer.
Repeated runs (up to seven times) in the Rheovibron clearly shows that E' and
T(1) temperature increase almost monotonically under these conditions. This

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*Note that considerable errors arise if these corrections are omitted. (See
 Appendix 1).

behavior is associated with morphological changes that occur within the sample. They match the enthalpy changes obtained from DSC measurements under similar circumstances.

In their torsional braid measurements, Connelly, et al.[27] found four distinct loss peaks, including a T(1) peak, for poly[bis(trifluoroethoxy) phosphazene]. These four peaks consisted of a secondary softening dispersion (at about −180°C), a primary softening dispersion, T(1) and Tm. From torsion pendulum measurements, Allen, et al.[26] also found a T(1) transition for this polymer evidenced by the drop in their G' curve, but their tan δ curves did not clearly show a distinct peak.

Figures 5 and 6 illustrate the E', E" and tan δ curves for the 1st and 3rd runs on well oriented (draw ratio x10) poly[bis(trifluoroethoxy)phosphazene]. This polymer has a much higher modulus than its unoriented counterpart (see Fig. 7). Although a decrease in the primary softening dispersion peak was expected here, it was not observed, which indicates that no substantial increase in crystallinity arises when the sample was oriented. This conclusion is supported by density measurements and heats of the T(1) transition mentioned later in this paper. Again, for this oriented polyphosphazene (compare Figures 5 and 6), an increase in E' and a decrease in the primary softening dispersion peak occur upon cycling the sample. In Fig. 8 for the unoriented poly[bis-(p-methlphonoxy)phosphazene] the primary softening dispersion occurs about 5°C and the T(1) transition is evident at 145°C approximately. This polyphosphazene shows a higher primary softening dispersion temperature than either samples 1 or 2 presumably because of its bulky side groups which tend to reduce the chain flexibility and raise the glass temperature.

Figure 9 depicts the E', E", tan δ curves of oriented poly[bis(p-methyl-phenoxy)phosphazene]. The broad T(1) transition region in this material may be associated with the broad bimodal molecular weight distribution found by

GPC analysis[29].

Moving now to polyphosphazene copolymers with and without chemically inert additives, some striking features are observed. For instance, E', E" and tan δ curves for unfilled and filled PNF (i.e., fluoroalkoxy-type) samples are shown in Figures 10 through 12. All of these crosslinked, rubbery specimens display a long plateau. Although filled PNF samples have much higher plateau levels (by as much as X10) than the unfilled polymer, yet only small differences are found between carbon black-filled and silica-filled PNF specimens. No T(1) transition is found for these hybrid copolymer samples (see Figures 10-13) because of their amorphous (or very low crystalline) nature. Note however, that double peaks (separated by more than 15°C) were observed in the primary softening dispersion regions for all of these copolymeric PNF samples studies. However, DSC scans only indicated a single glass transition, probably because the glass temperatures of homopolymer components are too close to each other to be resolved. The DSC method is unable to resolve two peaks that are close together. Elsewhere[30], it has been reported that the Rheovibron measurements succeeded where thermal methods failed for polysiloxane block copolymers. In general, it has been noted that the dynamic mechanical test provides one of the most sensitive probes for studying primary and secondary softening dispersions in polymers[31].

From torsional braid analysis for copolymers $[NP(OCH_2CF_3)(OCH_2C_3F_7)]_n$ and $[NP(OCH_2CF_3)(OCH_2(_3F_3 CHF_2)]_n$, Connelly and Gillham[27] also found two peaks 15° apart. These workers also reported the presence of two peaks in the logarithmic decrement vs. temperature plots of their $[NP(OCH_2CF_3)(OHC_2C_3F_7)]_n$ copolymer. Thermomechanical spectra of other phenoxy-type copolymers such as $[NP(OC_6H_5)(p-OC_6H_4C_2H_5)]_n$ also exhibit two loss peaks in the primary dispersion region[32]. This unusual behavior may be due to heterogeneities in the copolymer structure which obtain during synthesis. For instance, in the substitution of $[NP Cl_2]_n$ with two Alkoxides, some block copolymer character may result[27].

Other experiments[27] have been made on homopolymer blends to investigate polymer compatibility, as well as to simulate or probe the effects of possible irregularities in the copolymer strucutres. Contrary to expectation, only a single primary softening peak was observed. Contrariwise, Beres, et al.[33] have reported two Tg transitions in their DSC studies of two blends of aryloxyphosphazene homopolymers where the hompolymer Tg values were more than 20°C apart.

An analysis of the dynamic mechanical spectra of filled samples using simplified Mooney equation such as

$$E_f = E_o \ (1 + 2.5 \ \phi + 14.1 \ \phi^2) \tag{1}$$

where ϕ is the volume fraction of filler, E_o is the modulus of the unfilled sample, and E_f is the predicted modulus for filled material, are given in Table 3. Estimated values of E_f are based upon spherical, non-interacting particles. The differences noted in Table 3 may be attributed to uncertainties in the nature and shape of filler particles but more especially in the degree of crosslinking in these materials as provided by the manufacturer.

Mechanical spectra of APN (aryloxy-type) polyphosphazene containing alumina trihydrate filler, are illustrated in Fig. 13. They show a rather high storage modulus, E' in the glassy and rubbery plateau regions, some of which is due to the high filler content (150 phr; see Table 2).

In summary, the relative magnitudes of the changes in E' in each transition region, are tabulated in Table 4.

2. Differential Scanning Calorimetry

In Figure 14, the area of the endotherm at T(1) for poly[bis(trifluoroethoxy) phosphazene] increases appreciably with repeated sample cycling just above T(1), or by sample annealing in the vicinity of T(1). A gradual increase in the T(1)

temperature is also noted under these conditions. Annealing procedures such as these, are important in improving crystalline order within specimens.

Plots of the changes in T(1) and ΔH_1 (enthalpy change at T(1)) as a function of the number of heating cycles for unoriented poly[bis(trifluoroethoxy) phosphazene] are illustrated in Figures 15 and 16. Limiting T(1) temperatures as well as limiting heats of transition were determined from these plots to be $T(1)^{\infty} = 90.7°C$ and $\Delta H_1^{\infty} = 6.41$ cal/g respectively, based upon the notion that an asymptotic limits prevailed here.

The endotherm at T(1) for poly[bis(p-methylphenoxy)phosphazene] (not illustrated in the figures) showed a similar response to repeated temperature cycling through its T(1) of 154°C. The T(1) values and heats of T(1) transitions for this polymer are tabulated (see Tables 4 and 5).

Thermal analysis measurements were also made on the specimens measured in the Rheovibron. Results showed that both T(1) and ΔH_1 were enhanced during mechanical testing.

Whenever the poly[bis(trifluoroethoxy) phosphazene] sample is recrystallized by slow cooling from the molten state, a marked increase in the enthalpy occurs and the T(1) transition peak moves upwards by about 10°C. Changes in the magnitude and shape of these curves are shown in Figure 17. Note that the enthalpy change for the T(1) transition is about ten-fold greater than it is at Tm. Specific values of T(1) = 91°C, T_m = 241.5°C; $\Delta H(T(1))$ = 8.4 cal/g and $\Delta H(Tm)$ = 0.8 cal/g were found in the current investigation. Similar results have been reported[9,34] for this polymer. Whenever recrystallized samples were cycled repeatedly through Tm, decreases in these values were observed, maybe because   some polyphosphazenes are heat sensitive at or above their melting temperatures where they display some degree of degradation[34]. However these other authors did not subject their polyphosphazene to extensive high temperature cycling. Other thermal stability analysis[20,22,35] have been made on these

materials and more extensive work is in progress.

Recrystallization after heating above Tm usually produces needle-shaped crystallites instead well developed spherulites commonly encountered in melt crystallization or in solution cast films[34].

Furthermore it has been estimated that the volume changes at the two transitions are of the order of 4 to 6%. In Table 6 thermal analysis results are summarized and comparisons are made with other polymers which also show transitional changes in the solid state that are not mesomorphic in character.

Claims have been made from published X-ray diffraction studies on poly [bis(chlorophenoxy)phosphazene][37,38] that the T(1) transition involves a transformation from the orthorhombic crystalline structure with 3-dimensional order to a pseudo-hexagonal lattice exhibiting lateral order but longitudinal disorder. The lateral chain order is preserved above T(1), and this disappears completely above the higher first order (melting) transition. Recent broad-line NMR investigations claim that the disorder that exists above T(1) is dynamic rather than static in nature, and arises from the onset of rapid side-chain and backbone motions[39], although the writers of this paper believe that heterophase fluctuations may be responsible for some of the property changes that occur upon heating these polyphosphazenes. Much more experimental work is needed to elucidate the properties in relation to other polymeric structures, and to establish the extent and direction of chain motion. Equally important, the precise thermodynamics, volume changes, and kinetics of the transitions, at the T(1) and Tm transitions also require further study.

3. Glass Transition Temperatures

Tg values of the polyphosphazenes are reported in Table 7. No differences between oriented and unoriented polyphosphazene samples were detected. Each sample was measured at four different heating rates. The Tg corresponding to

1 °/min. heating rate was obtained by extrapolation from the $\ln(Tg)$ vs.
heating-rate plots. In general polyphosphazenes have lower Tg values than polymers
with organic-backbones. This is attributed to a flexible PN backbone, and a
comparatively large bond angles ($\widehat{NPN}$ = 119°, $\widehat{PNP}$ = 136°) compared to
C-C backbone polymers. The lack of substituents on nitrogen as well as the
flexibility imparted by the oxygen linkage from the phosphorus atom to the
substituent groups is also contributory. The alkoxy materials have even lower
Tg values consistent with the presence of the more flexible and less bulky
side groups in these polymers. A more restricted situation arises when alkyl
or aryl groups are linked directly to the phosphorus. Here measurably higher
Tg values are expected.

4. Density Measurement

Table 8 contains measured densities for samples #1 and #2 used in this
work. While repeated temperature cycling through the T(1) region (in the
Rheovibron) raised the density because of increased crystallinity, oriented
polyphosphazene samples did not indicate higher densities than those found
in their unoriented counterparts, presumably because of morphological changes
induced on drawing initially.

5. The T(1) Transition in Polyphosphazenes

Although this transition is associated with mesophase formation, there is
no definitive work that clearly shows that polyphosphazene homopolymers behave
as real liquids and not solids between the T(1) and Tm temperatures of respective
polymers. The dynamic mechanical properties presented in this paper are incapable
of solving this problem although considerable softening is noted above T(1) as
Connelly and Gillham[27] has also shown. The T(1) transition depends upon
heating or cooling rates, whereas a true relaxation process would be expected
to show no hysteresis response. On the other hand, the mechanical response of

polyphosphazenes is rather broad, and this may, to some extent, be associated with the broad molecular weight distribution of these polymers. For a thermodynamic transition, the nature and the arrangement of the substituents are both important factors since none of the polyphosphazenes with mixed substituents (i.e. copolymers) exhibited either T(1) (thermal) or a mechanical transition. X-ray diffraction measurements on APN and PNF samples showed no measurable amount of crystallinity. However, a small, but broad endothermic peak was noticeable in the PNF silica (filled) sample at 152°C but no peak(s) was found in APN copolymer . Its origin is not clear since this peak is intermediate between the T(1) and Tm transition encountered in the corresponding linear homopolymer. Although the absence of meridional X-ray [26,33] reflections and the persistence of equatorial x-ray reflections on going through the T(1) temperature has been interpreted to mean that disturbances occur only along the chain direction, more definitive measurements are still required since

alternative explanations are possible. Certainly, polyphosphazenes do not exhibit rod-like properties in solution with a Mark-Houwink exponent of 0.52

If indeed they really form true liquid crystals above T(1), it can be concluded that although rod-like polymers invariably gives rise to mesophase behavior, liquid crystal formation is not necessarily connected with stiff molecules, so that it still remains to establish beyond doubt, the true origin of the T(1) transition in polyphosphazenes.

6. Conclusions

The thermomechanical behavior of several polyphosphazenes have been determined from -120°C to 180°C approximately. The dynamic mechanical response of these materials is dominated by two transitional regions, namely (a) primary softening dispersion region (related to T_g) and (b) the so-called mesomorphic transition region (T(1)) which occurs between Tg and Tm.

It has been found that the relative magnitudes of the changes in E'
for some specimens may be as large as (X500) through the primary softening
dispersion, whereas changes as large as (X16) were found through the so-called
mesomorphic transition.

In the semicrystalline polyphosphazenes, the enthalpy of transition through
$T(1)$, ΔH_1, is about an order of magnitude higher than the change that occurs
upon melting. The change in $T(1)$ enthalpy is sensitive to temperature cycling and
asymptotically approaches a limiting value as the number of cycles tends to
infinity. Annealing enhances both crystallinity and sample modulus. Changes
in sample density were not found upon drawing but annealing did increase the
sample density. For filled polyphosphazenes, measured moduli could not be accounted
for using a simplified Mooney equation based upon filler level alone.

APPENDIX

When a sinusoidal tensile strain is applied to a viscoelastic sample, a
sinusoidal stress is generated within the sample. There is a phase lag, δ,
between the strain and the stress. The instrument output provides a measure
of the complex dynamic Young's modulus, E^*, as a function of frequency and
temperature. E^* is related to the storage modulus E' and loss modulus E'' of
the sample where

$$E^* = E' + iE''$$

and the ratio $E''/E'' = \tan \delta$, which is a measure of the stress-induced internal
friction found in the specimen. Consequently, useful information about the
internal molecular motions within the polymer are obtained as a function of frequency
and temperature. However, instrument and sample clamping correction, if
avoided, will give rise to considerable errors, especially when comparatively
soft elastomers are investigated. Only when these corrections to $|E^*|$ are made,
can the moduli and other parameters be derived with accuracy, using the equations

$$E' = |E*| \cos \delta$$

and
$$E'' = |E*| \sin \delta = E' \tan \delta.$$

Figure 18 clearly illustrates that very large discrepancies arise if these corrections are not undertaken for polyphosphazenes. As a precaution, they should be applied to all Rheovibron measurements as Massa[28] has already demonstrated. Certainly, they are most important for polyphosphazene and polysiloxane [30] elastomers.

ACKNOWLEDGMENT

FIGURE LEGENDS
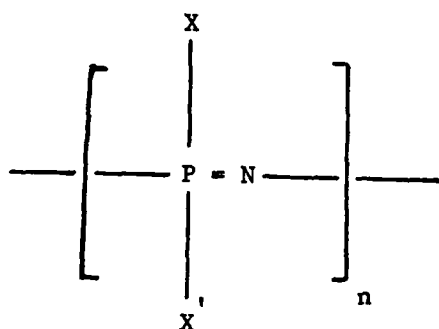
Figure 1   General Structure of polyphosphazenes where X and X' are aryloxy
              or alkoxy-type side groups of the same or different chemical structura
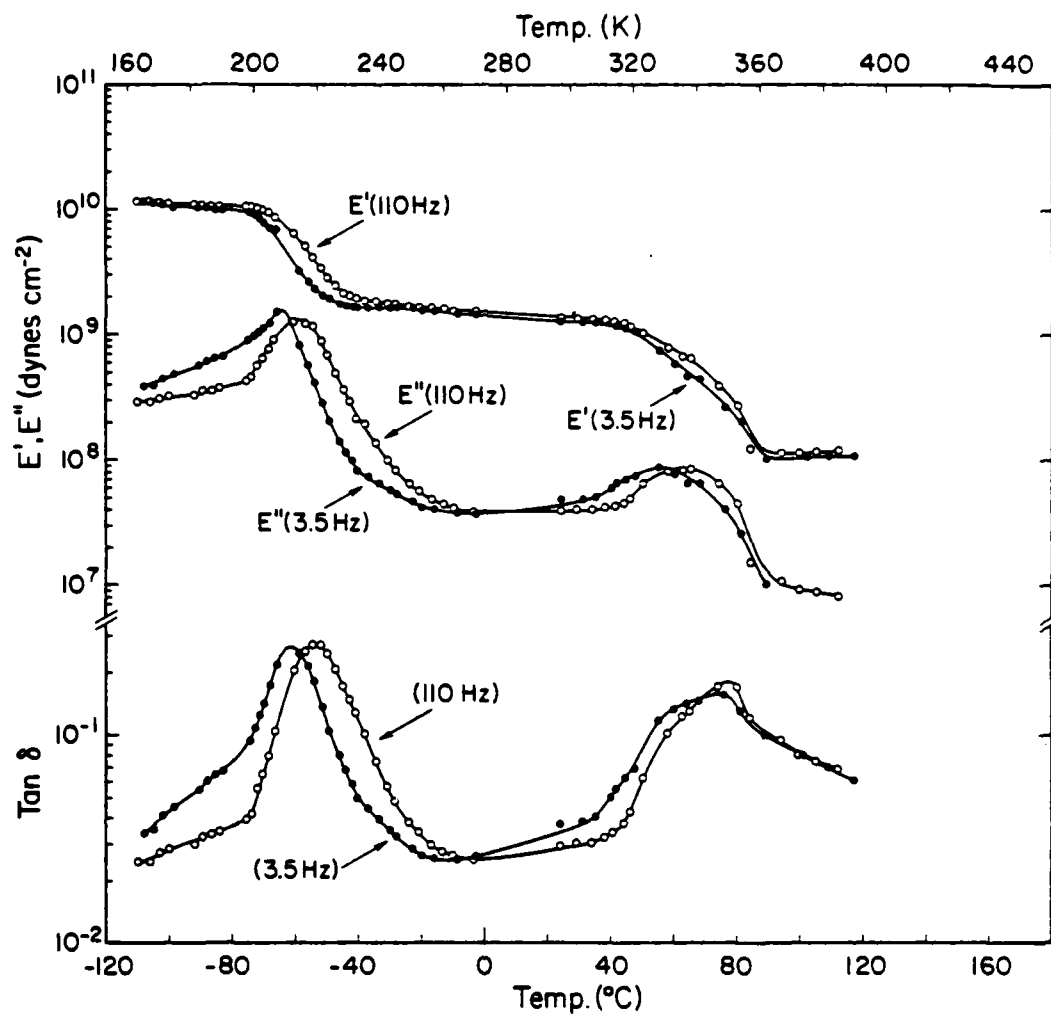
Figure 2   E', E" and tan δ of unoriented poly(bis(trifluo roethoxy)-
              phosphazene] versus temperature at 110 Hz and 3.5 Hz
              (1st run).

Figure 3   E', E" and tan δ of unoriented poly[bis(trifluoroethoxy)-
              phosphazene] versus temperature at 110 Hz and 3.5 Hz
              (7th run).

Figure 4   E', E" and tan δ curves of 1st run and 7th run poly[bis-
              (trifluoroethoxy)phosphazene], showing the effects of
              repeated temperature cycling through T(1) transition
              region (at 110 Hz).

Figure 5   E', E" and tan δ or oriented poly[bis(trifluoroethoxy)-
              phosphazene] vs. temperature at 110 Hz and 3.5 Hz
              (1st run).

Figure 6   E', E" and tan δ of oriented poly[bis(trifluoroethoxy)-
              phosphazene] versus temperature at 110 Hz and 3.5 Hz
              (3rd run).

Figure 7   E', E" and tan δ curves of unoriented and oriented poly-
              [bis(trifluoroethoxy)phosphazene] at 110 Hz.

Figure 8   E', E" and tan δ of unoriented poly[bis(p-methylphenoxy)-
              phosphazene] versus temperature at 110 Hz and 3.5 Hz.

Figure 9   E', E" and tan δ of oriented poly[bis(p-methylphenoxy)-
              phosphazene] versus temperature at 110 Hz and 3.5 Hz.

Figure 10   E', E" and tan δ of unfilled PNF sample versus temperature
              at 110 Hz and 3.5 Hz.

Figure 11   E', E" and tan δ of carbon black-filled PNF sample versus
              temperature at 110 Hz and 3.5 Hz.

Figure 12   E', E" and tan δ of silica-filled PNF sample versus
              temperature at 110 Hz and 3.5 Hz.

Figure 13   E', E" and tan δ of APN sample with alumina trihydrate
              filler versus temperature at 110 Hz and 3.5 Hz.

Figure 14   DSC curves showing the effect of thermal history on the
              T(1) endotherm for poly[bis(trifluoroethoxy)phosphazene].
              Heating rate, 5°/min; cooling rate between runs, 20°/min.
              Runs 1 through 10).

Figure 15   Plots of T(1) temperature versus no. cycles and reciprocal
              of no. cycles for unoriented poly[bis(trifluoroethoxy)-
              phosphazene]. Heating rate, 5°/min.; cooling rate between
              runs, 20°/min.

FIGURE LEGENDS (Continued)

Figure 16   Heat of transition at T(1), ΔH_1 plotted against no. cycles and reciprocal no. cycles for unoriented poly[bis-(trifluoroethoxy)phosphazene].

Figure 17   DSC scan for the comparison of the endotherms at T(1) and T_m for poly[bis(trifluoroethoxy)phosphazene]. Heating rate, 20°/min. The sample was recrystallized from the melt at 252°C .

Figure 18   Corrected and uncorrected curves of the dynamic Youngs moduli, E^* , and the δ for the unfilled fluoroalkoxy type polyphosphazene. Sample description is given in Table 2.

$$\overline{} \left[\overline{} \underset{\underset{X'}{|}}{\overset{\overset{X}{|}}{P = N}} \overline{} \right]_n \overline{}$$

Figure 1. General Structure of Poly(phosphazenes) where X and X'
are aryloxy ar alkoxy type side groups of the same or
different chemical structure.

FIGURE 2. E', E" and Tan δ of unoriented poly[bis(trifluoro ethoxy)-
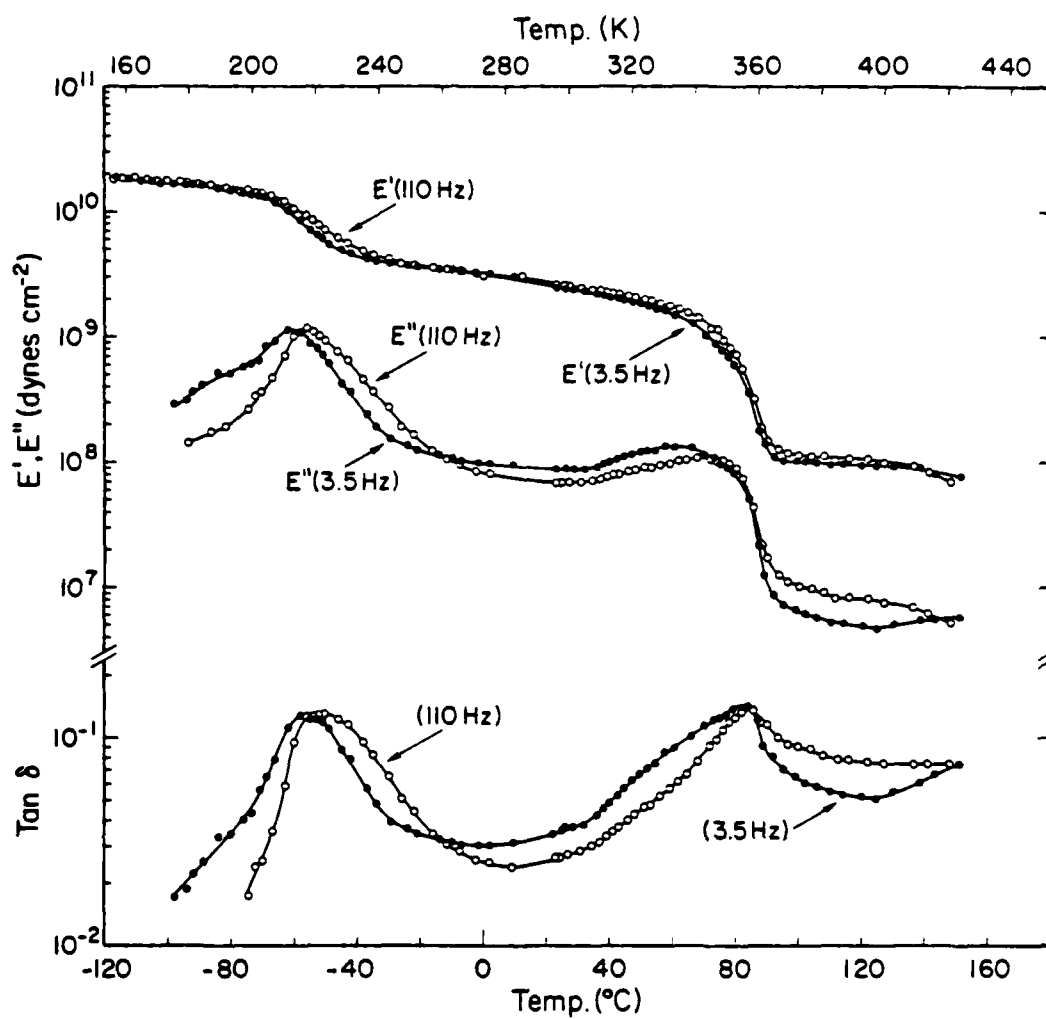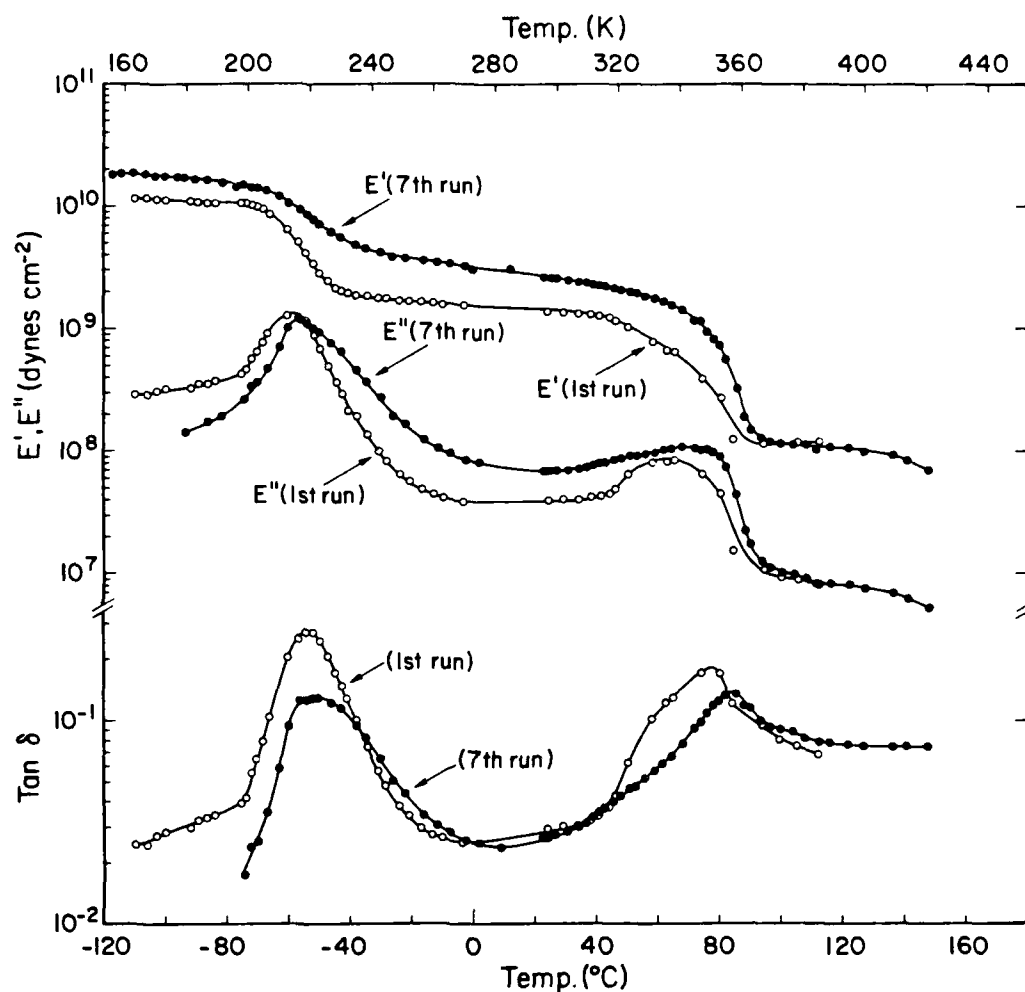phosphazene] versus temperature at 110HZ and 3.5HZ (1st run).

FIGURE 3. E', E'' and Tan δ of unoriented poly[bis(trifluoro-ethoxy)phospha-zene] versus temperature at 110 HZ and 3.5 HZ (7th run).

Figure 4. E', E" and tan δ curves for the 1st and 7th runs for poly
[bis(trifluoroethoxy)phosphazene], showing the effects of
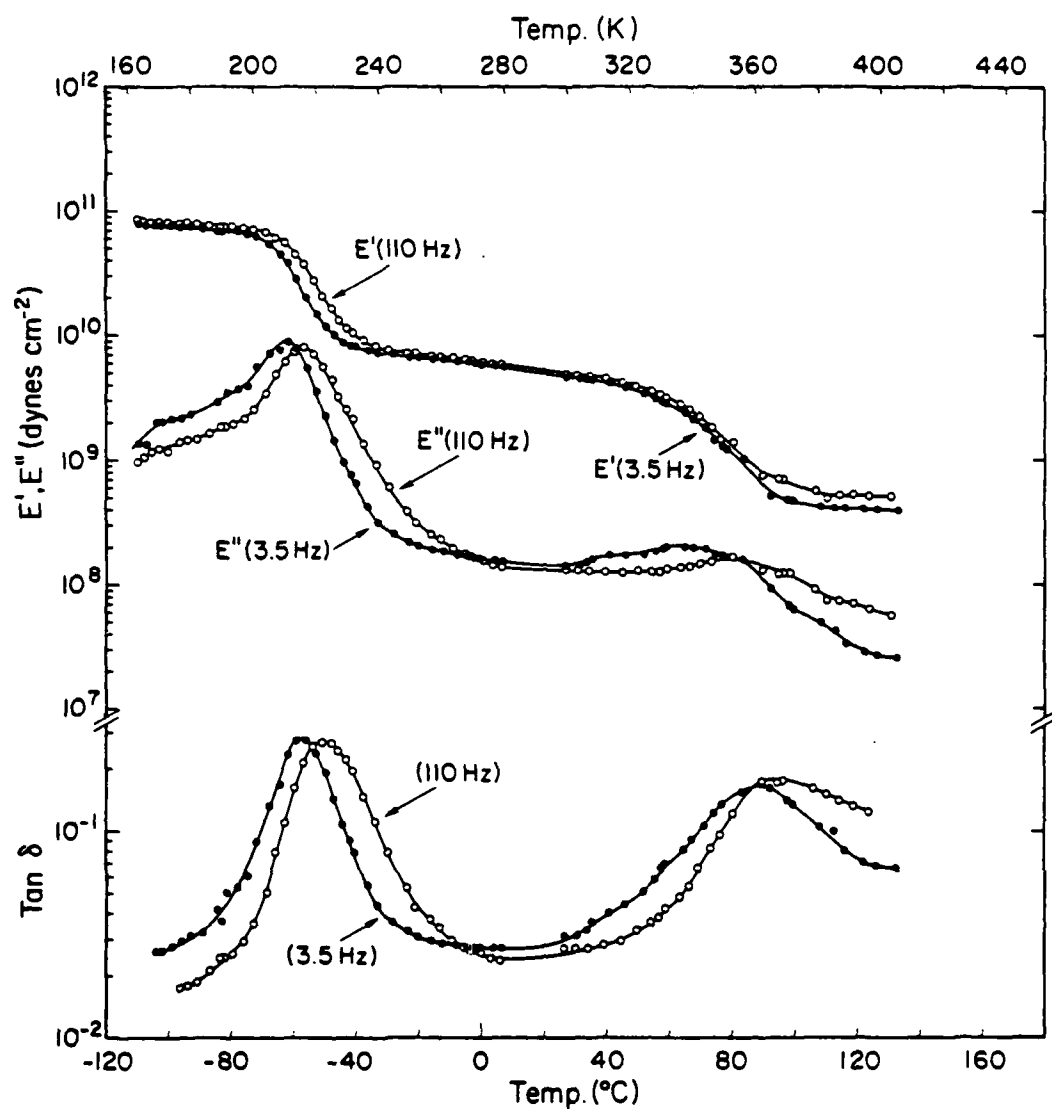repeated temperature cycling through the T(1) region (at 110 Hz).

FIGURE 5. E', E" and Tan δ of oriented poly[bis(trifluoroethoxy)phospha-
zene] temperature at 110 Hz and 3.5 Hz (1st run).

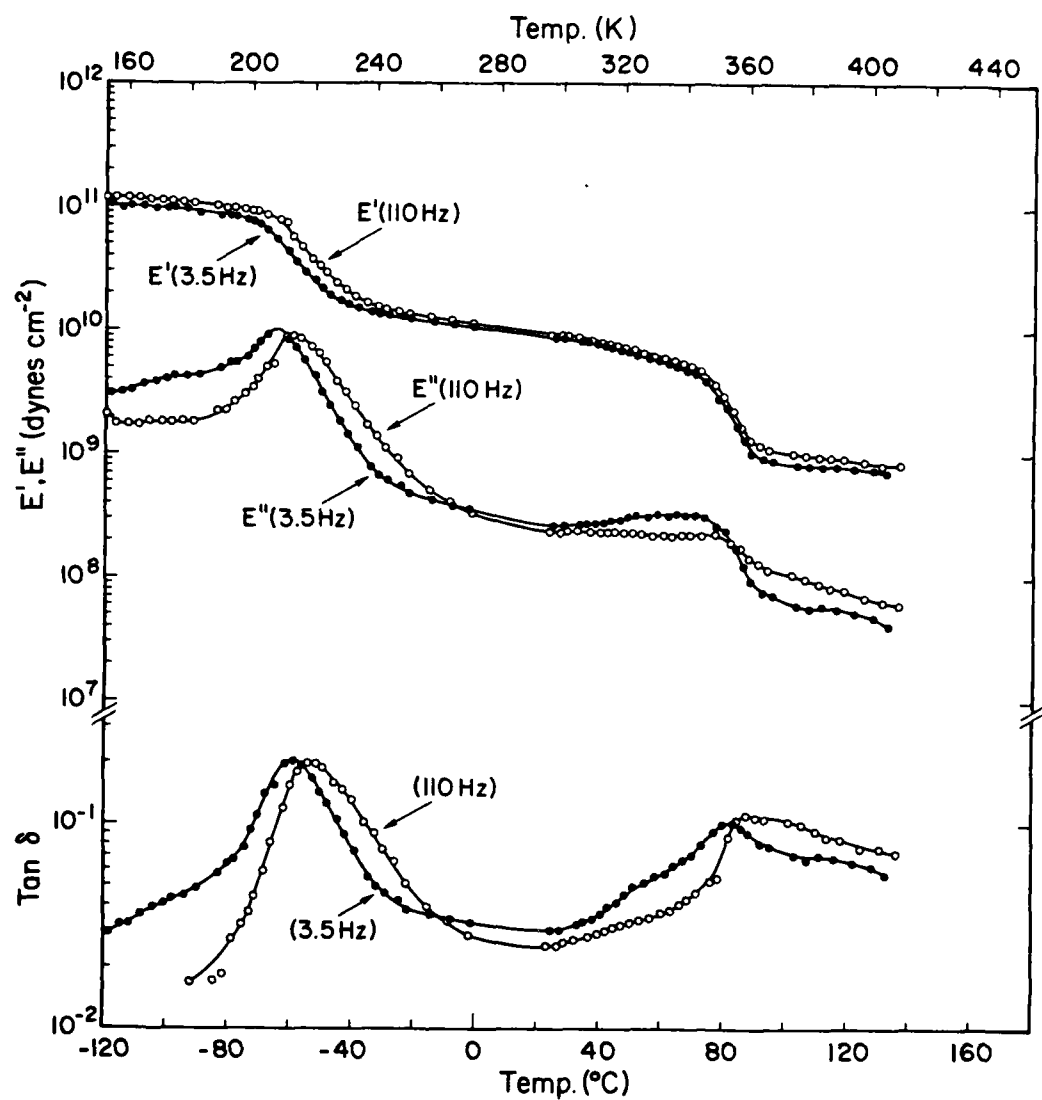Figure 6   E', E" and tan δ of oriented poly[bis(trifluoroethoxy)-
            phosphazene] versus temperature at 110 Hz and 3.5 Hz
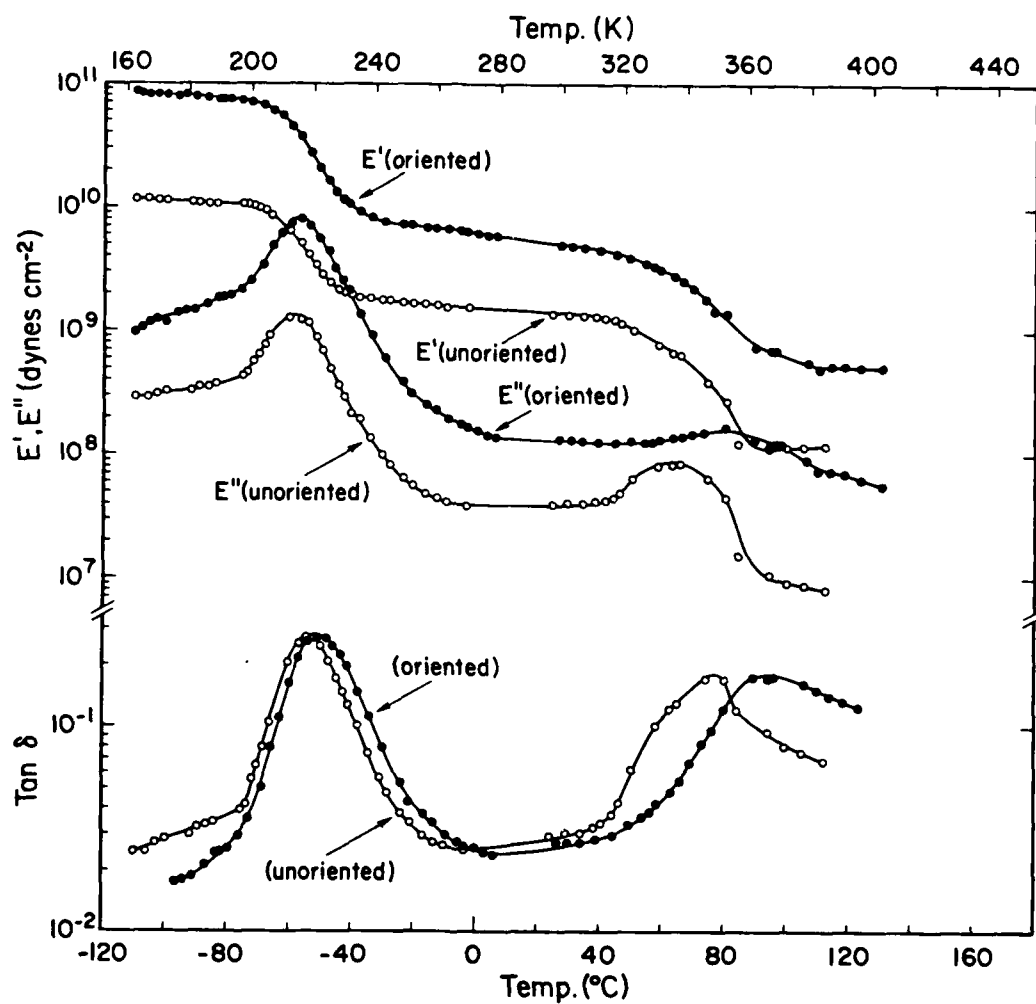   (3rd run).

Figure 7   E', E" and tan δ curves of unoriented and oriented poly-
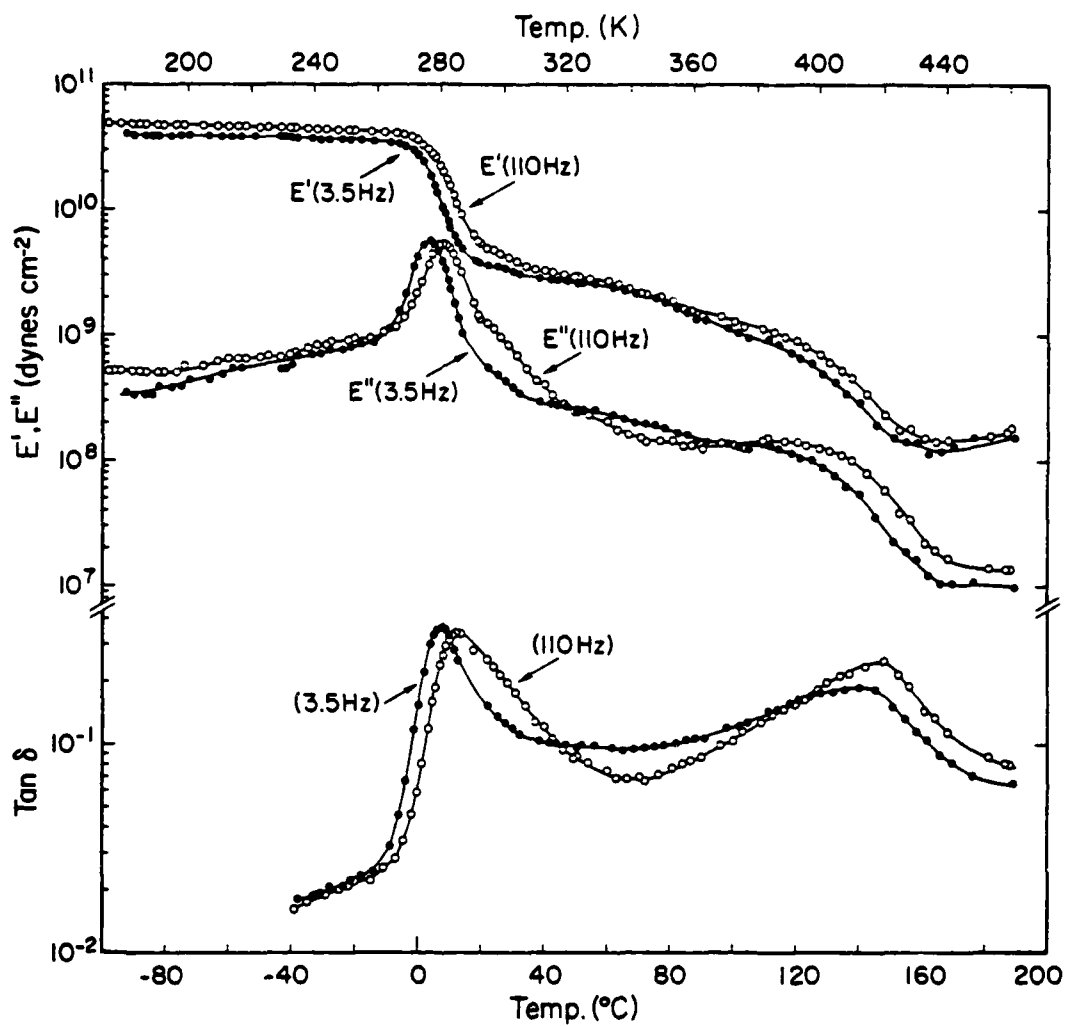[bis(trifluoroethoxy)phosphazene] at 110 Hz.

FIGURE 8.   E', E" and Tan δ of unoriented poly[bis(p-methyl phenoxy) phosphazene] versus temperature at 110 HZ and 3.5 HZ.
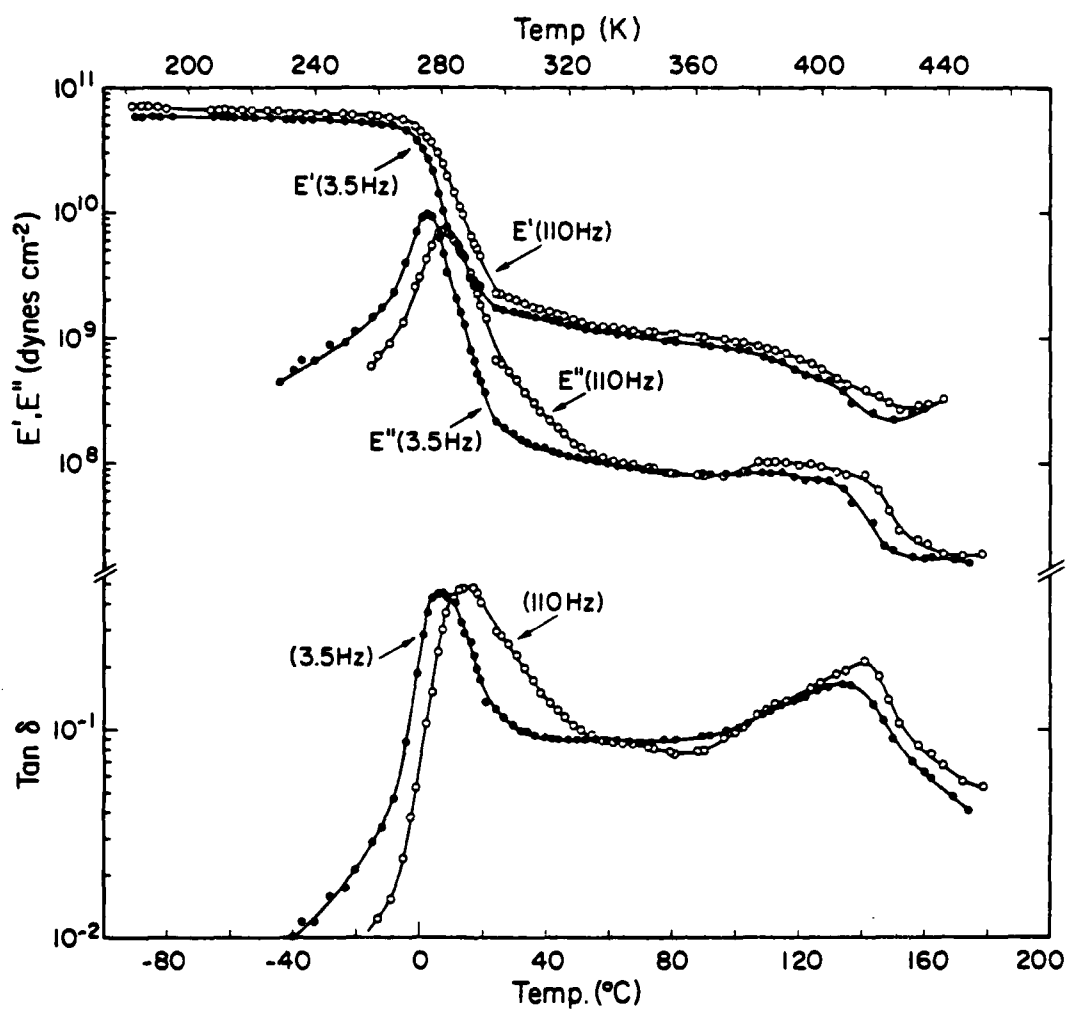
FIGURE 9. E', E" and Tan δ of oriented poly[bis(p-methylphenoxy)phosphazene] versus temperature at 110 HZ and 3.5 HZ.
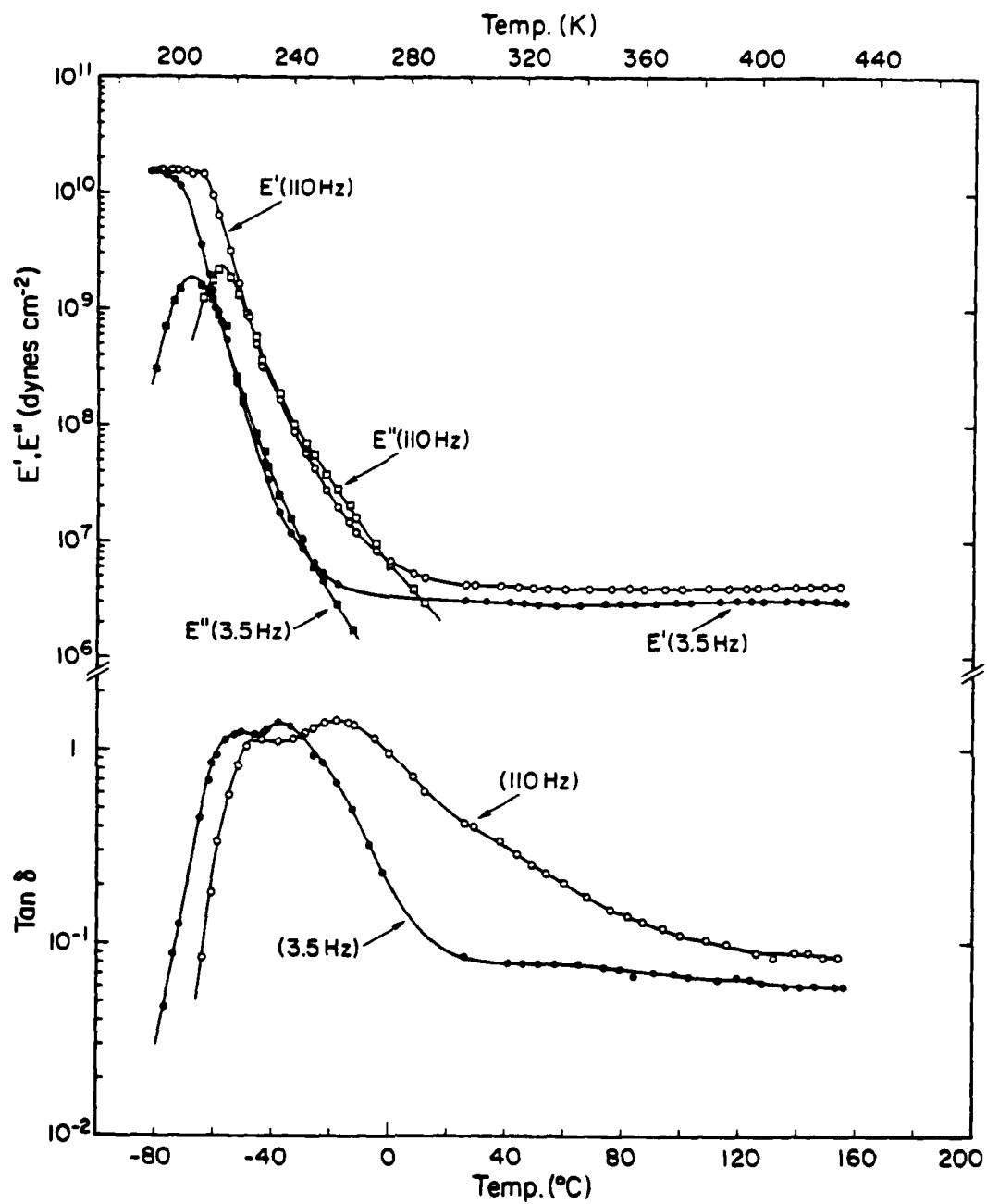
FIGURE 10   E', E'' and Tan δ of unfilled PNF sample versus temperature at
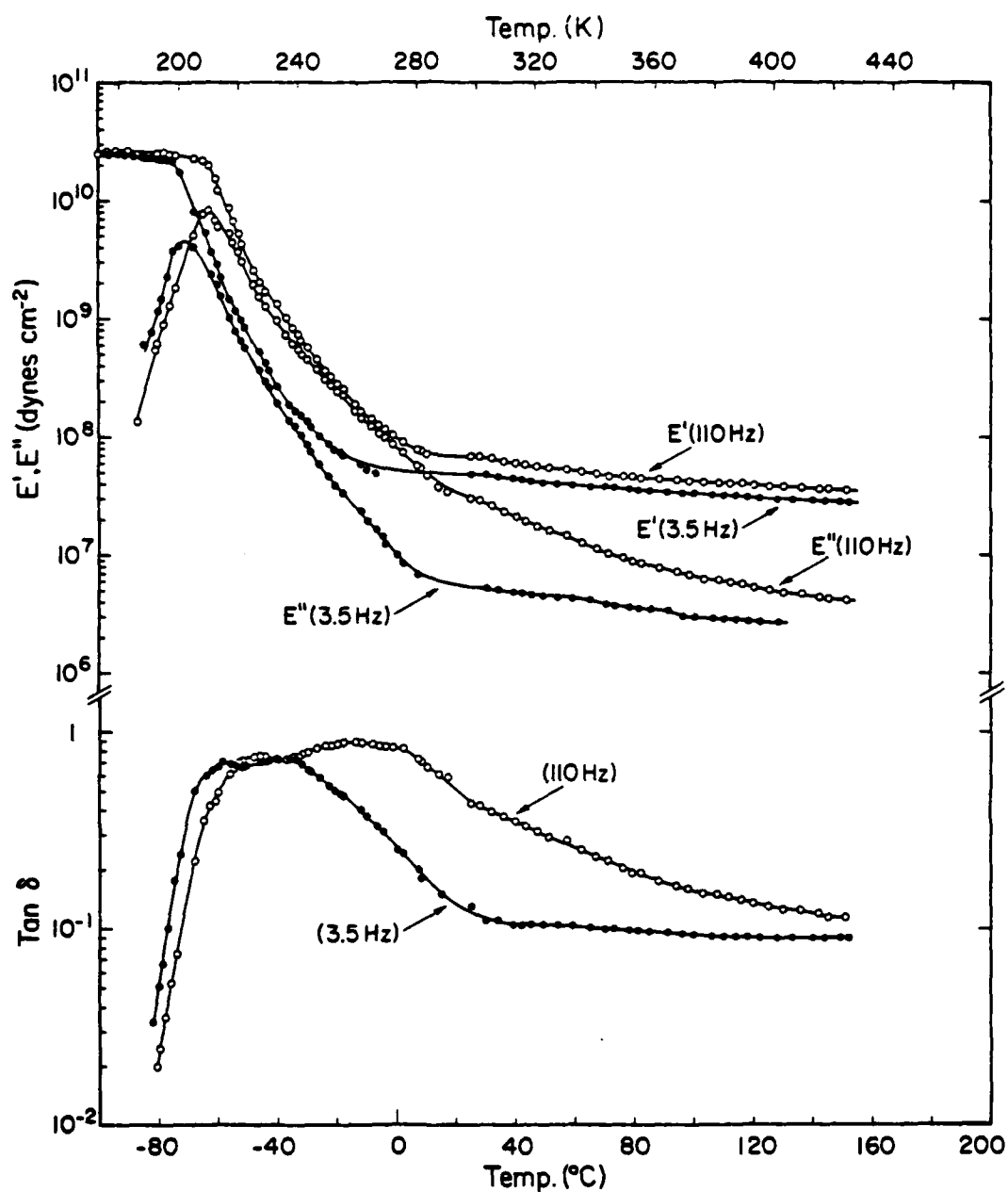110 Hz   and 3.5 Hz.

FIGURE 11   E', E" and Tan δ of carbon black-filled PNF sample versus
temperature at 110 Hz and 3.5 Hz.

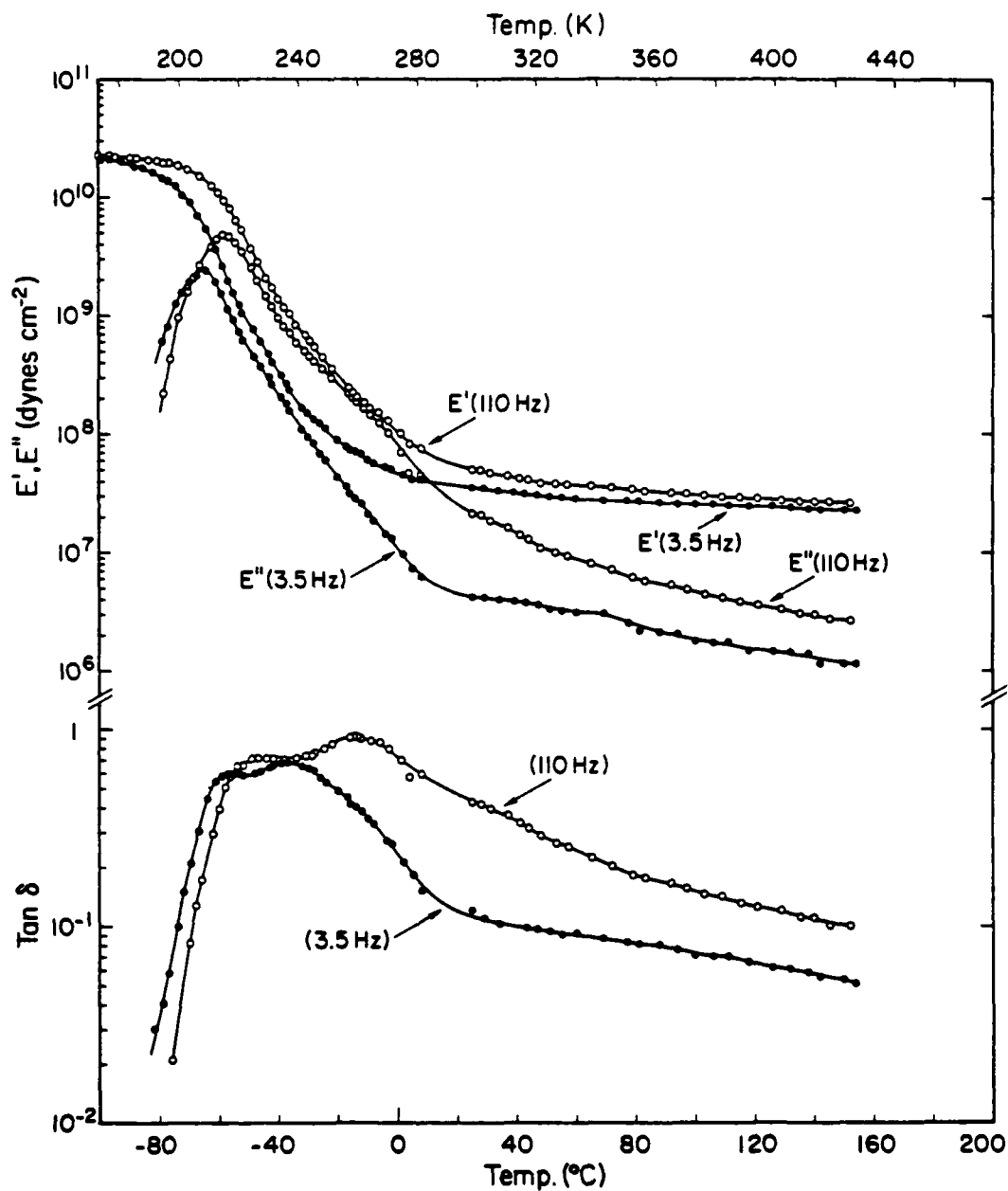FIGURE 12. E', E'' and Tan δ of silica-filled PNF sample versus temperature at 110 Hz and 3.5 Hz.

FIGURE 13 E', E" and Tan δ of APN sample with alumina trihydrate filler versus temperature at 110 H₂ and 3.5 H₂.

FIGURE 14. DSC curves showing the effect of thermal history on the T(1) endotherm for poly[bis(trifluoroethoxy)phosphazene]. Heating rate, 5°/min; cooling rate between runs, 20°/min. (Runs 1 through 10).

FIGURE 15. Plots of T(1) temperature versus No. cycles and reciprocal of No. cycles for unoriented poly[bis(trifluoroethoxy) phosphazene] Heating rate, 5°/min., cooling rate between runs, 20°/min.

FIGURE 16. Heat of transition at T(1), ΔH_2 plotted against No. cycles and reciprocal of No. cycles for unoriented poly[bis(trifluoroethoxy) phosphazene].
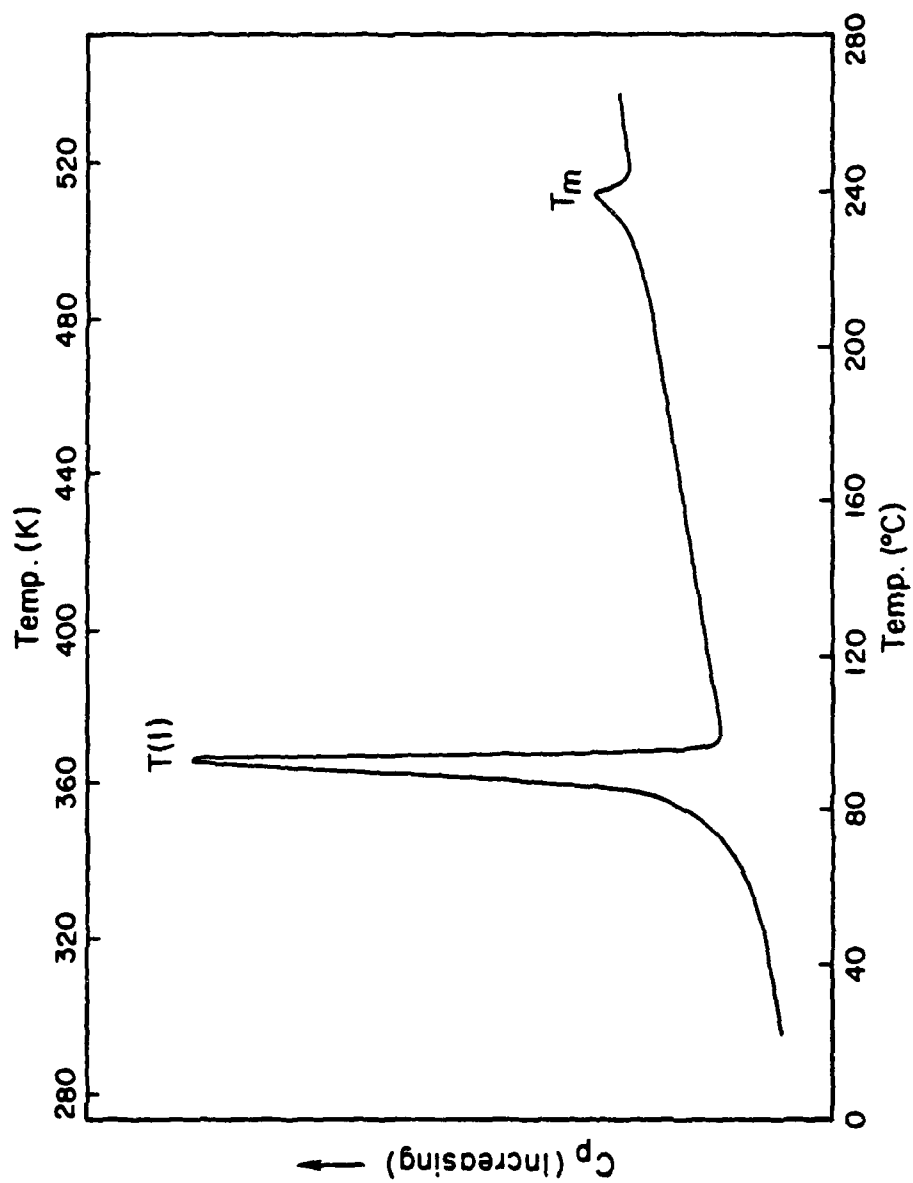
FIGURE 17. DSC scan for the comparison of the endotherms at T(1) and Tm for poly[bis(trifluoroethoxy)phosphazene]. Heating rate, 20°/min. The sample was recrystallized from the melt (at 252°C).
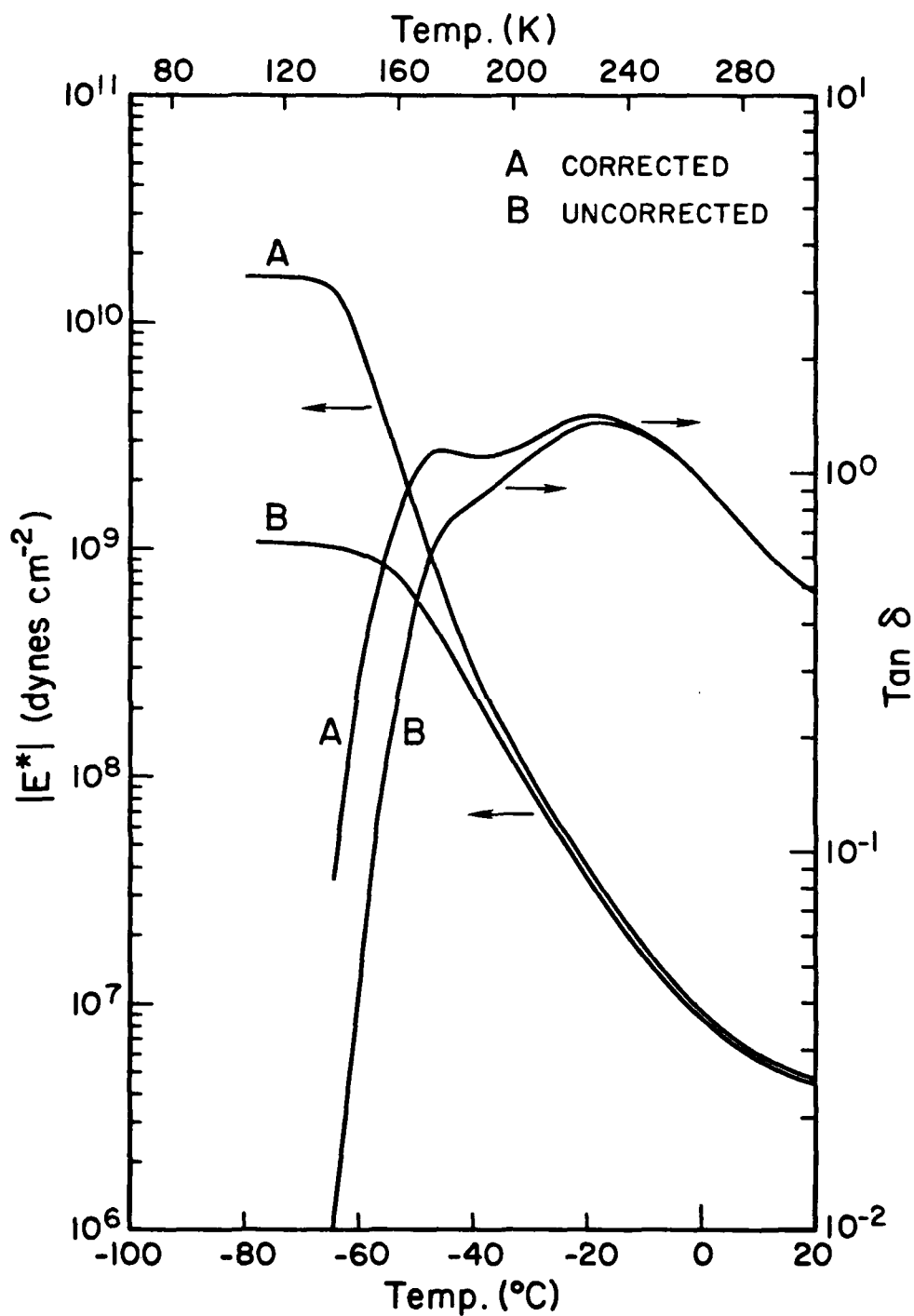
Figure 18 Corrected and uncorrected curves of the dynamic Youngs moduli,
          E*., and tan δ curves for the unfilled fluoralkoxy type poly-
          phosphazene. Sample discription is given in Table 2.

TABLE LEGENDS

Table 1   Description of Homopolymers

Table 2   Description of Unfilled and Filled Copolymers of Polyphosphazenes.

Table 3   Dynamic Young's Modulii of Filled Samples (Measured and Predicted).

Table 4   Changes in E' in the primary softening and T(1) transition regions.

Table 5   T(1) Temperature and Heat of Transition, ΔH_1, at T(1) for Poly[bis(trifluoroethoxy)phosphazene] for Oriented and Unoriented Specimens.

Table 6   T(1) Temperature and Heat of Transition, ΔH_1, at T(1) for Poly[bis(p-methylphenoxy)phosphazene] for Oriented and Unoriented specimens.

Table 7   Comparison of Thermal Transition Data for Polyphosphazenes and other polymers.

Table 8   Glass Transition Temperatures of Polyphosphazenes.

Table 9   Density of Polyphosphazenes.

TABLE 1.   Description of Homopolymers

Sample (#/type)		Substituents	Description	Source
1	Poly [bis(trifluoro-ethoxy)phosphazene]	CF_3CH_2O-	Sheet-form	Allcock Penn State Univ.
2	Poly [bis(p-methyl-phenoxy)phosphazene]	$P-CH_3C_6H_4O-$	Sheet-form $\overline{M}n=4.79 \times 10^5$ $\overline{M}w=3.51 \times 10^6$	Army Materials & Mechanics Research Center

TABLE 2. Unfilled and Filled Copolymers of Polyphosphazenes

| Sample Number | Manufacturer Code No. | Substituents | | Filler | | Description |
		Type	Mole %	Material	Parts per 100 (wt %)	Sample Type and Other Remarks
3	K-19298 PNF-200^R	CF_3CH_2O Other fluoro-alkoxy side groups	65 35	Unfilled	----	Sheet form, radiation vulcanized. No anti-oxidant added to samples 3 through 5.
4	R-209152	CF_3CH_2O Other fluoro-alkoxy side groups	65 35	Carbon Black	30	Sheet form, filled stock. Peroxide vulcanized.
5	R-209153	CF_3CH_2O Other fluoro-alkoxy side groups	65 35	Silica	30	Sheet form, filled stock. Peroxide vulcanized.
6	R-210147 APN^{TM}	Ph-O P-EtPhO $O-CH_2=CHC_6H_4O$	49.1 41.3 9.6	Alumina Trihydrate	150	Sheet form, filled sulfur-cured.

* Samples 3 – 6 were obtained from Firestone Tire & Rubber Company.

TABLE 3. Dynamic Young's Modulus (Measured and Predicted)
          of Filled Polyphosphazene Samples

Material	Temp(°C)	E*-measured (dynes/cm^2)	E*-predicted (dynes/cm^2)
Carbon black-filled	25	6.8×10^7	8.9×10^6
PNF (sample #4)	50	5.5×10^7	8.5×10^6
Silica-filled	25	4.7×10^7	7.4×10^6
PNF (sample #5)	50	3.8×10^7	7.1×10^6

Table 4. Changes in E' in the primary softening and T(1)
          transition regions

Sample (#/type)	Condition	$\Delta E'$ (PSD*)	$\Delta E'$ T(1)[+]
1. Poly[bis(trifluoro-ethoxy)phosphazene]	1. Unoriented (1st run)	x 9	x10
	2. Unoriented (7th run)	x 5	x16
	3. Oriented (1st run)	x11	x12
	4. Oriented (2nd run)	x10	x10
2. Poly[bis(p-methyl-phenoxy)phosphazene]	1. Unoriented	x20	~ x12
	2. Oriented	x70	~ x 5
3. Unfilled PNF	Unoriented	x460	--
4. Carbon black-filled PNF	Unoriented	x370	--
5. Silica-filled PNF	Unoriented	x370	--
6. APN with alumina trihydrate	Unoriented	x110	--

*PSD = Primary Softening Dispersion
+T(1) = Mesomorphic Transition

Table 5. Mesomorphic transition temperature T(1) and Heat of transition,
ΔH_1, at T(1), for poly[bis(trifluoroethoxy) phosphazene] for
oriented and unoriented specimens.

No. cycle	T(1) °C		ΔH_1 (cal/g)	
	Unoriented*	Oriented[+]	Unoriented*	Oriented[+]
1	76.3	76.1	2.97	4.37
2	78.5	77.1	4.98	4.87
3	79.3	77.1	5.33	5.11
4	79.3	–	5.51	5.17
5	–	77.8	–	5.39
6	79.8	78.1	–	5.44
7	80.0	–	5.97	5.46
8	–	78.3	–	5.54
9	80.3	–	6.03	–
10	80.5	–	6.08	–
∞[#]	$T(1)^{\infty}$=80.7	$T(1)^{\infty}$=79.1	$\Delta H_1^{\infty} = 6.41$	$\Delta H_1^{\infty} = 5.78$

*Heating rate = 5°/min., cooling rate between runs=20°/min.
+Heating rate = 20°/min., cooling rate between runs-20°/min.
#Obtained by extrapolation to infinite no. of cycle.

Table 7. Comparison of Thermal Transition Data for polyphosphazenes and other polymers (Ref. 36).

Sample	$T(1)$ (°C)	T_m (°C)	$\Delta H(T(1))$ (cal/g)	$\Delta H(T_m)$ (cal/g)	$\Delta V(T(1))$ %	$\Delta V(T_m)$ %
Poly[bis(trifluoro-ethoxy)phosphazene]	92	240	8.6	0.8	5	6
Poly[bis(p-chloro-phenoxy)phosphazene]	169	356	6.6	0	3.5	5.7
Poly(diethyl-siloxane)	-5	20	2.4	0.36	-	-
Polyethylene	-	141	-	68	-	15
Poly(tetrafluoro-ethylene)	-	327	-	13.7	-	20

TABLE 8   Glass Transition Temperatures

Sample (# / type)	T_g* (°C)
1 Poly [bis(trifluoroethoxy)phosphazene]	−66
2 Poly [bis(p-methylphenoxy)phosphazene]	0
3 Unfilled PNF	−62
4 Carbon black-filled PNF	−64
5 Silica-filled PNF	−63
6 APN sample (alumina trihydrate-filled)	− 9

* T_g values for 0°/min (i.e., infinitely slow) heating rate were obtained by extrapolating data of higher heating rates to eliminate artifacts due to heating.

TABLE 9   Density of Polyphosphazenes

(1)   Poly[bis(trifluoroethoxy)phosphazene]

Sample	Condition	Density (g/ml)
Unoriented	1) As received 2) After 7th run in Rheovibron	1.695 1.715
Oriented	3) As drawn 4) After 2nd run in Rheovibron	1.692 1.707

(2)   Poly[bis(p-methylphenoxy)phosphazene]

Sample	Condition	Density (g/ml)
Unoriented	1) As received 2) After 1st run in Rheovibron	1.247 >1.247
Oriented	3) As drawn	1.244

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